

Reactive adsorption of sulfur compounds in diesel on nickel supported on mesoporous silica

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Abstract

Sulfur compounds in commercial diesel were selectively removed by reactive adsorption using metallic nickel nanoparticles supported on mesoporous silica. Nanosize nickel particles were supported on mesoporous silica SBA-15 and KIT-6 by impregnation of nickel nitrate and subsequent reduction. X-ray diffraction and transmission electron microscopy study revealed that the maximum nickel concentration achieved was 30 wt% for both the substrates, before particle agglomeration sets. Under these conditions, the best dynamic adsorption capacity observed was 1.7 mg/g at 10 ppmw S breakthrough level with a high sulfur diesel (240 ppmw) on 30 wt% Ni/SBA-15. For a low sulfur diesel (11.7 ppmw), the corresponding result was 0.47 mg/g for the same adsorbent at 0.1 ppmw S breakthrough level, which is suitable for fuel cell applications.

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1. Introduction

The production of transportation fuel with low sulfur concentration has been a major concern in petroleum industry due to the stringent statutory environmental regulations imposed by the government worldwide [1,2]. For example, the Korean government has already announced a plan to reduce the upper limit of sulfur concentration in diesel to 10 ppmw by 2009 [2]. To date, conventional hydrodesulfurization (HDS) to convert the sulfur compounds into hydrogen sulfide using Co–Mo/Al₂O₃ or Ni–Mo/Al₂O₃ catalysts has been a major desulfurization process which failed to meet expected sulfur regulation, while HDS with unsupported transition metal sulfide still seems to be the only practical solution to achieve low sulfur diesel less than 10 ppmw [3–5]. However, further reduction of sulfur concentration by HDS, to less than 1 ppmw, is still a challenging research target. In addition to the environmental aspect, the demand for ultra-low sulfur diesel (ULS-diesel), less than 0.1 ppmw, has been growing due to the fuel cell applications. Transportation fuels, such as gasoline, jet

fuel, and diesel, are ideal fuels due to their high energy density, ease of storage and transportation, and established distribution network. However, their sulfur concentration must be less than 0.1 ppmw to protect the deactivation of catalysts in reforming process and electrodes in fuel cell system [6].

Recently, adsorptive desulfurization has been reported to be a complementary and alternative technique for HDS [7]. Metal ion exchanged Y zeolites showed high selectivity and capacity for sulfur compounds using π -complexation between metal ion and sulfur compounds [7–10]. However, their selectivity and capacity for sulfur compounds varied depending on the fuel composition, such as aromatic and moisture concentrations [11]. Unlike π -complexation, the reactive adsorption of sulfur compounds, adsorption assisted by chemical reaction between metal particles and adsorbates, was reported on metallic nickel supported on silica, which could lower sulfur level in model diesel or fractionated jet fuel to below 10 ppmw [12–14]. In reactive adsorption, fuel composition is not expected to affect the selectivity and adsorption capacity for sulfur compounds, because specific bond formation reaction between sulfur atom and metal in adsorbent is the main driving force for sulfur compounds adsorption. Our group explored the possibility of the production of low sulfur diesel using nickel particles supported on mesoporous silica SBA-15 and observed that the

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surface status of nickel particles played a critical role in reactive sulfur adsorption [15,16].

The present paper describes the results of the extension of the above studies to achieve ULS-diesel with sulfur levels less than 0.1 ppmw from commercial diesel feedstock.

2. Experimental

2.1. Chemicals

All chemicals were used as received without further purification. Pluronic 123 (P123), tetraethoxysilane (TEOS), *n*-butanol, and tetrahydrofuran (THF) were obtained from Aldrich. Hydrochloric acid solution (HCl) and nickel nitrate hexahydrate were obtained from Junsei. Two grades of commercial diesel, high sulfur diesel (HS-diesel) and low sulfur diesel (LS-diesel) with 240 and 11.7 ppmw, respectively, were purchased from gas station near Daejeon.

2.2. Preparation of adsorbents

Mesoporous silica SBA-15 and KIT-6 were synthesized based on the methods reported elsewhere [17,18]. For the synthesis of SBA-15, 2.0 g of P123 was dissolved in 15 g of deionized water and 80 g of 2 M HCl solution. Then, 4.25 g of TEOS was added and this mixture was stirred for 5 min and then kept at 308 K for 1 day, followed by aging for another 24 h at 373 K. The solid product was filtered without washing, dried in an oven at 373 K, and subsequently calcined in O₂ flow for 4 h at 823 K. For the synthesis of KIT-6, typically, 3.2 g of P123 and *n*-butanol were dissolved in 116 g of deionized water and 6.3 g of 35 wt% HCl solution under stirring at 305 K. TEOS was added into the resultant solution at 308 K and the magnetic stirring was continued for 24 h at the same temperature. Subsequently, the mixture was placed in an oven at 373 K for 24 h. The remaining steps in synthesis procedure were the same as for SBA-15. On SBA-15 and KIT-6, Ni(NO₃)₂·6H₂O dissolved in THF was impregnated by incipient wetness method. THF is better than deionized water in terms of the nickel particle dispersion [15]. The solids thus obtained were dried in an oven at 373 K with N₂ purging for 1 h and then reduced in hydrogen gas flow at 873 K for 4 h. The resultant samples were designated as Ni/SBA-15 and Ni/KIT-6, respectively.

2.3. Characterization of the adsorbents

The BET surface area, pore volume and pore size distribution of calcined mesoporous silica (SBA-15 and KIT-6) were measured by nitrogen adsorption at 77 K using a Micromeritics (ASAP 2010) surface area measurement apparatus. Pore size distribution was calculated by Barrett–Joyner–Halenda (BJH) method. X-ray powder diffraction (XRD) patterns and transmission electron microscopy (TEM) images of Ni/SBA-15 and Ni/KIT-6 were obtained using Rigaku Miniflex (Cu K α radiation (λ = 0.15406 nm) at 30 kV) and EM912 EF-TEM operated at 120 kV in Korea Basic Science Institute.

2.4. Breakthrough experiments

A constant flow liquid metering pump was used to feed diesel to experimental set-up for the breakthrough test. One gram of adsorbent was packed in a stainless steel column with 4 mm inner diameter and 300 mm length. Total bed volume occupied by 1.0 g of adsorbent was 2.7 ml. Appropriate particle size in the range 37–44 μ m, was obtained by sieving the materials. Tubular furnace was equipped for heat treatment and temperature maintaining. The moisture in hydrogen gas was removed prior to use by 3A zeolite. The feed flow rate was maintained at 0.2 ml/min. Thus mean residence time of the fluid was 13.5 min and liquid hourly space velocity (LHSV) was 4.44 h⁻¹. The sulfur concentration of eluted diesel was measured by a total sulfur analyzer (9000LLS, Antek). Quantitative analysis of sulfur compounds in the diesel feeds were performed using HP 6890 series gas chromatograph (GC), equipped with SUPELCO 24158 SPB-1 SULFUR capillary column and a flame photometric detector (FPD). Identification of the sulfur compounds was carried out using the standard model compound solutions.

For the breakthrough test with HS-diesel, 10 ppmw was taken as the criterion for sulfur breakthrough. We defined two adsorption capacity terms as follows. When the sulfur concentration of eluted diesel reaches 10 ppmw, the volume of eluted diesel so far was defined as the breakthrough volume, based on which the breakthrough sulfur adsorption capacity was estimated. On the other hand, total sulfur adsorption capacity was defined as the integrated area between the breakthrough curve and the straight line, representing the initial sulfur concentration of the feed.

3. Results and discussion

3.1. Properties of adsorbents

Fig. 1 displays the low angle X-ray diffraction patterns of calcined mesoporous silica SBA-15 and KIT-6. Based on the

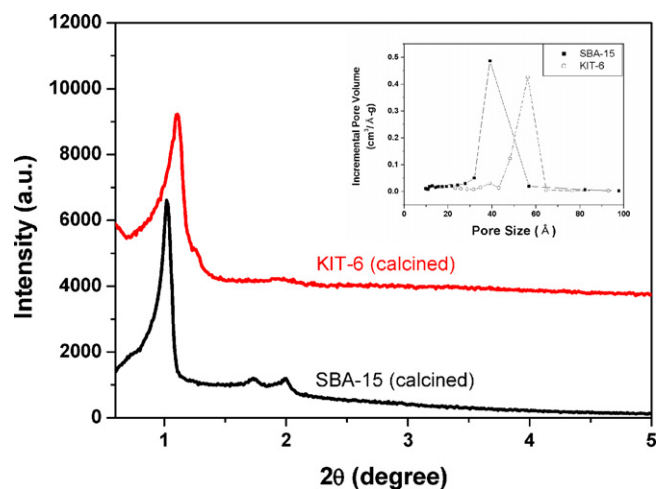


Fig. 1. X-ray diffraction patterns of SBA-15 and KIT-6: low angle region for mesopore characterization (inset shows pore size distributions of calcined SBA-15 and KIT-6 by BJH method).

Table 1
Physical properties of substrates obtained from N₂ adsorption at 77 K

Properties	SBA-15	KIT-6
BET surface area (m ² /g)	672	670
Total pore volume ^a (cm ³ /g)	1.08	1.16
Average pore diameter ^b (nm)	6.4	5.4

^a Total pore volume at $P/P_0 = 0.98$ (P : partial pressure of N₂ at 77 K, P_0 : 1 atm, saturated N₂ pressure at 77 K).

^b Average pore diameter was calculated with the equation $4V/A$, where V is the total pore volume at $P/P_0 = 0.98$ and A is the BET surface area.

previous reports, the shapes and positions of the well-defined XRD peaks reveal that SBA-15 has hexagonally packed one-dimensional pore structure and KIT-6 has bi-continuous cubic three-dimensional pore structure [15,16]. Table 1 also summarizes the surface area, average pore size, and pore volume of mesoporous silica SBA-15, KIT-6 obtained by nitrogen adsorption at 77 K. Table 1 shows that both SBA-15 and KIT-6 have large surface area and similar average pore size. The main difference between KIT-6 and SBA-15, derived from Fig. 1, is the pore structure, which consists of one-dimensional linear channel in SBA-15 and three-dimensional branched channel network in KIT-6.

On these mesoporous silica substrates, nickel particles were supported by impregnation and subsequent reduction in H₂ environment. The status of the nickel particles on mesoporous silica was investigated by XRD at high angle region, 20–70°, as shown in Fig. 2. As the concentration of nickel increased, the intensity of peaks corresponding to metallic nickel increased regardless of types of mesoporous silica. When the nickel concentration in adsorbent is below 30 wt%, XRD peaks for metallic nickel are too broad to be noticed. Low intensity XRD peaks analyzed using Scherrer equation show that nanosize nickel particles, smaller than 5 nm, are formed on the surface of mesoporous silica. At the nickel concentration of 40 wt%, high intensity and sharp peaks corresponding to metallic nickel (111) and (200) appeared. This means that higher concentration of nickel precursor might induce the formation of nickel crystallites larger than 10 nm. The TEM images in Fig. 3 confirm the observation made by XRD. TEM images of 30 wt% Ni/KIT-6 and 30 wt% Ni/SBA-15 show that nickel nanoparticles smaller than 5 nm are evenly distributed on mesoporous silica KIT-6 and SBA-15. On 40 wt% Ni/KIT-6 and 40 wt% Ni/SBA-15, nickel crystallites of size larger than 10 nm are observed, suggesting that agglomeration of nickel particles occurred outside the mesoporous structure of the silica. As the formation of large particles at higher nickel concentration, 40 wt%, reduces the surface adsorption sites of nickel particles, it is expected to be a disadvantage for sulfur compounds adsorption.

3.2. Sulfur compounds adsorption with HS-diesel

Fig. 4 shows the sulfur adsorption breakthrough curves of HS-diesel on 30 wt% Ni/SBA-15 at various adsorption temperatures. As the boiling range of commercial diesel is around 523–623 K, adsorption temperature was limited to

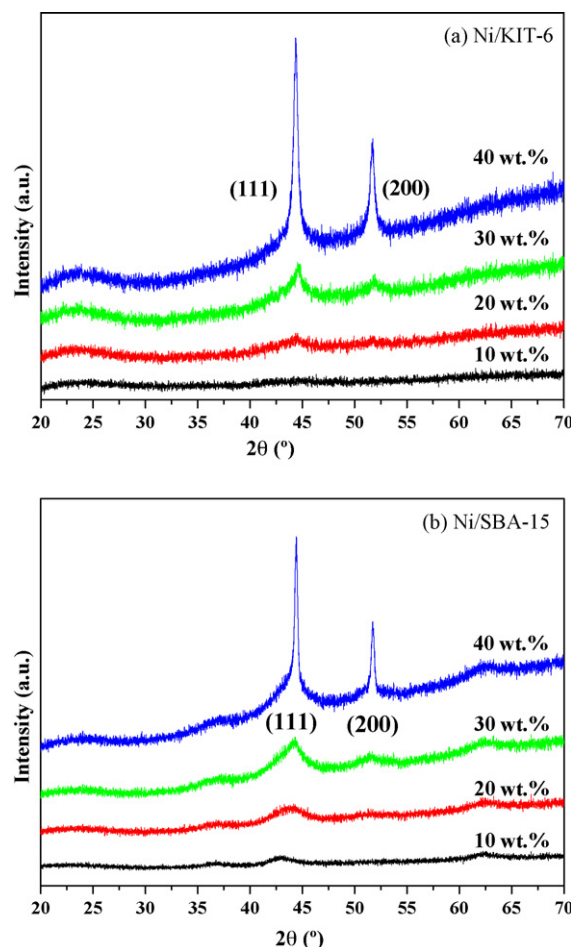


Fig. 2. X-ray diffraction patterns of Ni/KIT-6 and Ni/SBA-15 depending on the nickel concentration: (a) Ni/KIT-6 and (b) Ni/SBA-15.

473 K to prevent or minimize the loss of feed by vaporization. At room temperature, 298 K, sulfur compounds breakthrough occurred almost immediately after the feed solution was eluted, and the sulfur concentration in breakthrough curve increased gradually. This means that 30 wt% Ni/SBA-15 does not adsorb the sulfur compounds effectively at room temperature. At 473 K, however, the sulfur compounds were removed completely until the eluted volume was 5 ml/g, and the breakthrough of sulfur compounds occurred at 9 ml/g. The enhancement of sulfur compounds adsorption at elevated temperature strongly suggests that the interaction involved between the nickel incorporated adsorbent and the sulfur compounds should be chemisorption. Song and coworkers have made a similar observation, but did not provide any data for temperature-dependent sulfur adsorption [12]. They suggested that reactive adsorption was the main reason for the removal of the sulfur compounds in fractionated jet fuel because nickel particles supported on aluminosilica removed sulfur compounds at higher temperature (493 K). From our experimental results and previous report, it can be concluded that chemisorption or reactive adsorption is the major mechanism for this system.

In addition to the size of metallic nickel particles and their temperature-dependent reactivity toward sulfur compounds,

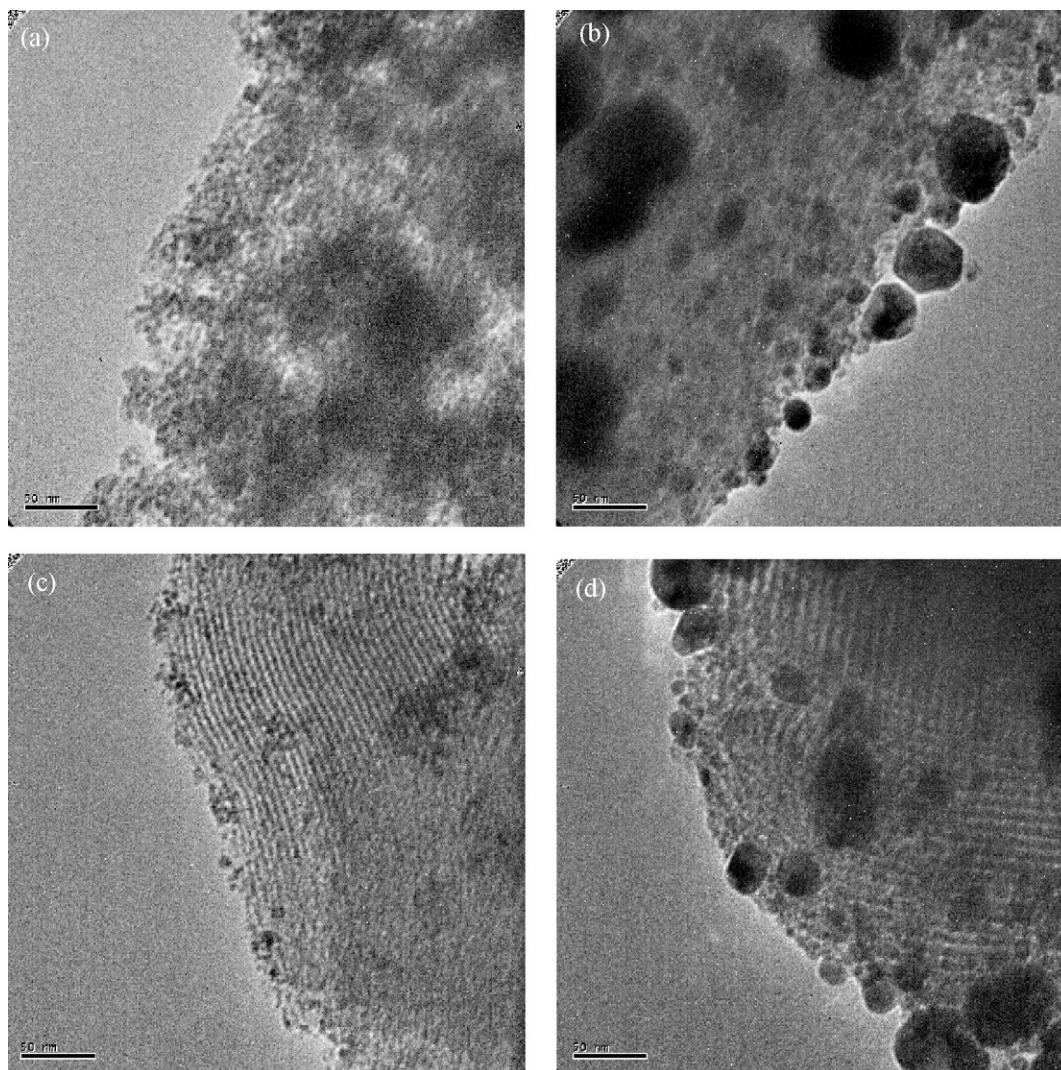


Fig. 3. Transmission electron microscopy images of (a) 30 wt% Ni/KIT-6, (b) 40 wt% Ni/KIT-6, (c) 30 wt% Ni/SBA-15, and (d) 40 wt% Ni/SBA-15: scale bars indicate the length of 50 nm.

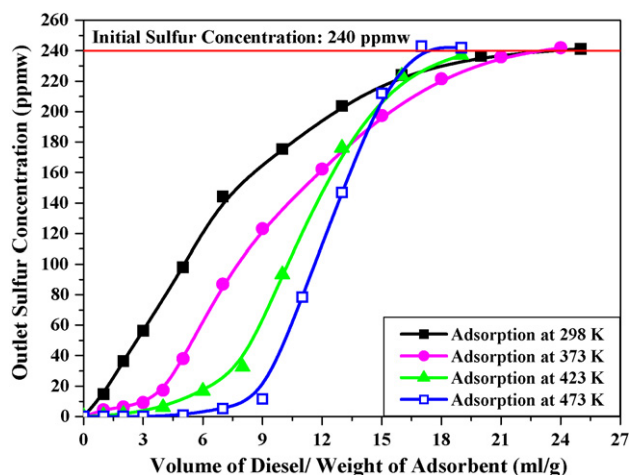


Fig. 4. Breakthrough curves of 30 wt% Ni/SBA-15 depending on the adsorption temperature: HS-diesel (240 ppmw sulfur) was used as feed solution.

pore structure might be an important factor to control sulfur adsorption. Fig. 5 shows the dependence of sulfur breakthrough on the type of mesoporous substrates. As the nickel concentration of both adsorbents, Ni/KIT-6 and Ni/SBA-15, increased from 10 to 30 wt%, the breakthrough volume also increased. However, the breakthrough volume for both adsorbents decreased drastically at 40 wt%, even to a value smaller than that at 10 wt%. As discussed in Figs. 2 and 3, the nickel particle agglomeration at high nickel concentration seems to be the main reason for the drastic decrease of the breakthrough volume. Thus, 30 wt% was taken as the optimum nickel concentration for the maximum sulfur adsorption capacity of both Ni/KIT-6 and Ni/SBA-15. Nevertheless, the shape of breakthrough curves and the volume of adsorption capacity of each adsorbent were quite different depending on the substrates. As shown in the bar chart of Fig. 6, the breakthrough capacity of Ni/SBA-15 was larger than that of Ni/KIT-6 at the same nickel concentration. At 30 wt% Ni concentration, these values were 1.7 and 1.0 mg/g of the adsorbents, respectively. However, the total sulfur adsorption

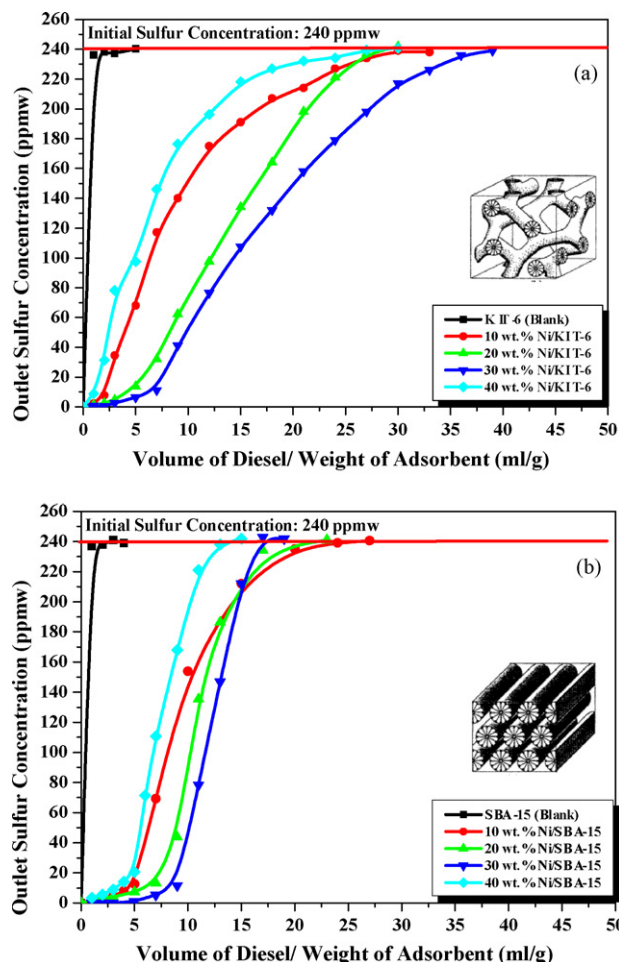


Fig. 5. Breakthrough curves of Ni/KIT-6 (a) and Ni/SBA-15 (b) depending on the nickel concentration at 473 K: HS-diesel (240 ppmw sulfur) was used as feed solution.

capacity of Ni/SBA-15 was smaller than that of Ni/KIT-6 at a given nickel concentration. The difference between breakthrough and total sulfur adsorption capacity might be attributed to the nature of pore connectivity in the one-dimensional pore structure of SBA-15 and three-dimensional pore structure of KIT-6. The larger breakthrough adsorption capacity of Ni/SBA-15 compared to that of Ni/KIT-6 suggests that one-dimensional straight channel is more suitable for the sulfur compounds diffusion than three-dimensional branched, curved channel. On the other hand, the higher total sulfur adsorption capacity of Ni/KIT-6 than that of Ni/SBA-15 at the same nickel concentration might be explained by the pore blockages. Although SBA-15 has a large pore size around 6 nm, linear channel structure of SBA-15 might be vulnerable to pore blockage because of the formation of nickel particles at the pore mouths with the diameter around 6 nm. In this case, nickel particles located deep inside from the entrance are not accessible to the sulfur molecules in diesel. However, pore blockage might be less in KIT-6 because of better access provided by the branched network to the nickel particles located in the internal surface.

In Fig. 7, the composition change of sulfur species in eluted diesel was investigated by GC-FPD. In the original commercial diesel used in this experiment, various types of sulfur

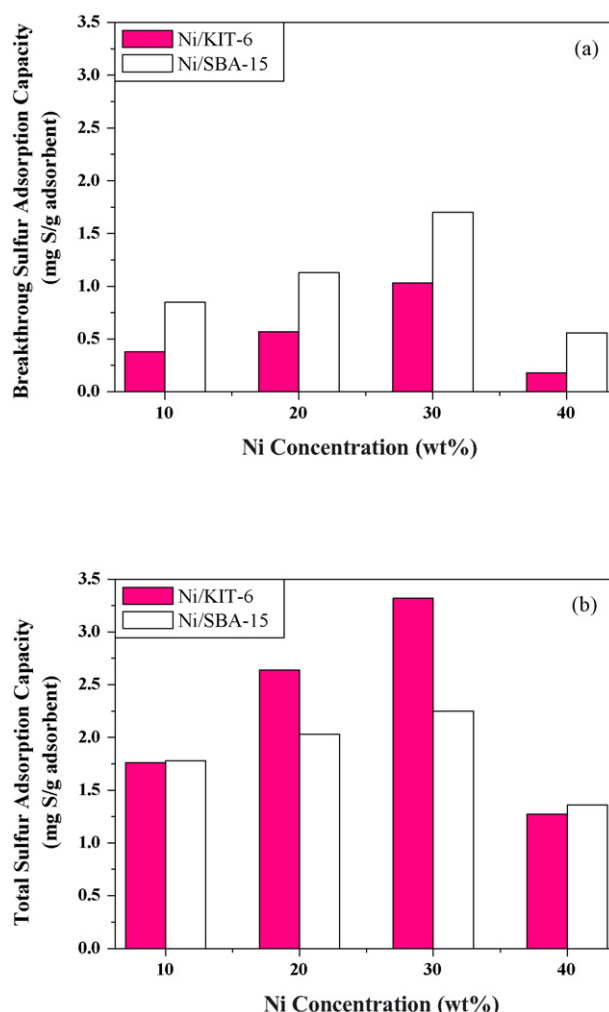


Fig. 6. Breakthrough sulfur adsorption capacities (a) and total sulfur adsorption capacities (b) of Ni/KIT-6 and Ni/SBA-15 depending on the nickel concentration at 473 K: HS-diesel (240 ppmw sulfur) was used as feed solution.

compounds were co-existed from low molecular weight sulfur compounds, such as benzothiophene (BT), to high molecular weight alkyl-substituted dibenzothiophene (R-DBT), for example 4,6-dimethyldibenzothiophene (4,6-DMDBT) and so on. Each sulfur compound was identified by comparing its retention time with its standard compound. As shown in Fig. 7(e), the retention times of BT and 4,6-DMDBT were 17 and 49 min. Fig. 7(a) does not display any peaks for sulfur compounds until the effluent diesel volume was 5 ml/g. The sulfur concentration at that point was below 1 ppmw by total sulfur analyzer. When the eluted volume was 9 ml/g (Fig. 7(c)), total sulfur concentration was 11.6 ppmw and major sulfur compounds in eluted diesel at 9 ml/g were 4,6-DMDBT and higher molecular weight R-DBTs. Although the sulfur concentration increased to 78.4 ppmw at 11 ml/g (Fig. 7(d)), any peaks for alkyl-substituted BTs were not observed. This indicates that nickel particles on mesoporous silica show higher selectivity toward small sulfur molecules, such as BTs, than high molecular weight refractory sulfur compounds, such as, 4,6-DMDBT and their alkyl-substituted derivatives, due to their steric hindrance. As the sulfur–nickel direct interaction is the

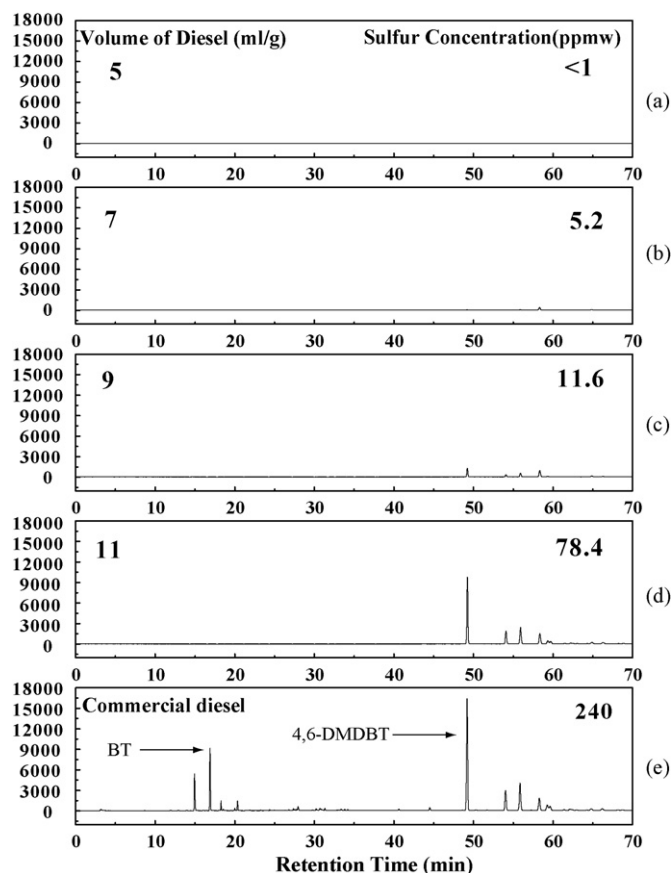


Fig. 7. Gas chromatograms for the change of sulfur species in eluted diesel: adsorbent was 30 wt% Ni/SBA-15 and HS-diesel (240 ppmw sulfur) was used as feed solution.

main interaction for reactive adsorption, a preference for low molecular weight sulfur compounds due to steric hindrance seems to be inevitable. To increase selectivity toward high molecular weight, refractory sulfur compounds, a smaller size of nickel particles dispersed on mesoporous silica should be preferable.

3.3. Production of ULS-diesel using Ni/SBA-15

Although three-dimensional pore structure in Ni/KIT-6 enhanced total sulfur adsorption capacity, one-dimensional channel in Ni/SBA-15 with fast diffusion might be more important for the production of low sulfur concentration diesel with less than 10 ppmw. Based on the experimental results, optimum amount of metallic nickel supported on mesoporous silica with one-dimensional channel structure, 30 wt% Ni/SBA-15, was selected as an adsorbent for the production of ULS-diesel. Of late, low sulfur commercial diesel (ca. 10 ppmw) is generally available in the gas station because of the environmental regulations in Korea. Thus, commercial diesel with 11.7 ppmw sulfur, LS-diesel, was selected as feed solution to produce ULS-diesel. As shown in Fig. 8, 50 ml of LS-diesel was converted into ULS-diesel (<0.1 ppmw) by 1.0 g of adsorbent, giving a breakthrough adsorption capacity

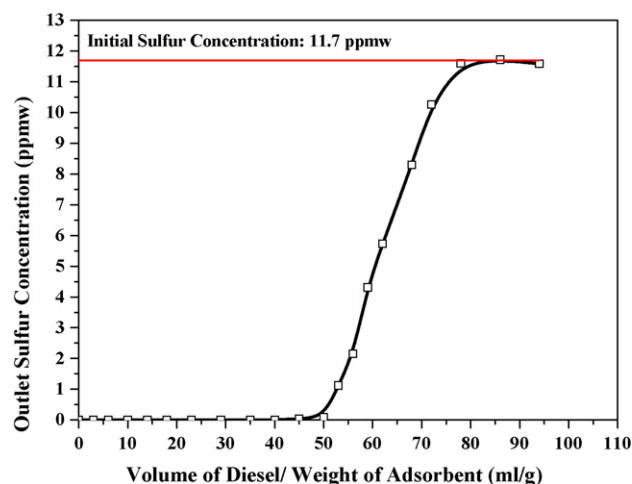


Fig. 8. A breakthrough curve of 30 wt% Ni/SBA-15 at 473 K: LS-diesel (11.7 ppmw sulfur) was used as feed solution.

of 0.47 mg/g. According to the weight limitation of 10 kg adsorbent in fuel desulfurizer set by U.S. Department of Energy, this adsorbent would purify 500 l of LS-diesel into ULS-diesel [19]. The achievement in this work can be applied for both mobile and stationary purpose immediately, in case of finding an effective regeneration method for adsorbent. Thus, our next research target should be focused on adsorbent regeneration.

4. Conclusions

Metallic nickel nanoparticles supported on mesoporous silica KIT-6 and SBA-15 were prepared to produce ULS-diesel, which is suitable for fuel cell applications. Investigation of these adsorbents by XRD and TEM revealed that nanosize nickel particles were formed and evenly distributed on mesoporous silica. Breakthrough test with HS-diesel showed that sulfur adsorption capacity of adsorbent was maximized depending on nickel concentration and pore structure of substrates. Optimized adsorbent produced ULS-diesel with less than 0.1 ppmw from LS-diesel.

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